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<b>(21) International Application Number:</b> PCT/FI97/00404 <b>(22) International Filing Date:</b> 24 June 1997 (24.06.97) <b>(30) Priority Data:</b> 962612 24 June 1996 (24.06.96) FI <b>(71) Applicant (for all designated States except US):</b> BOREALIS POLYMERS OY [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> IDELMANN, Peter [FI/FI]; Talvikkitie 24 C 19, FIN-01300 Vantaa (FI). PALMQVIST, Ulf [SE/SE]; Vestergårdsvägen 19, S-44441 Stenungsund (SE). MÜNSTEDT, Helmüt [DE/DE]; Waldweg 16, D-91054 Buckenhof (DE). <b>(74) Agent:</b> NESTE OY; Patent Services, P.O. Box 310, FIN-06101 Porvoo (FI).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ANTIFOULING COATING  <b>(57) Abstract</b>  An antifouling coating for reactors, vessels, lines or other equipment, which are exposed to gaseous or liquid monomers or polymer powders comprise a coating selected from polysulfone (PS) or polyethersulfone sulphone (PES) and polyetherimide (PEI). The coating may have a thickness of 0.1-3 mm, preferably 0.3-2 mm. Preferably the coating is filled with one or more substance giving antistatic properties.		

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## Antifouling coating

- 5 The present invention concerns antifouling coating for vessels, lines or other equipment exposed to liquid or gaseous mediums or powders causing fouling of the surfaces. Especially the invention concerns an antifouling coating for reactors, lines and equipment used in the polymerization art.
- 10 Reactor fouling is a known problem for example in polymerizing olefins. The build-up of the polymer on the surfaces of the polymerization reactor decreases productivity and interferes with the quality of the end product. Several solutions to avoid this problem have been developed. One solution is to polish the surfaces of the reactor or line in order to avoid polymer adhesion. However, this kind of polishing is very expensive and the effect
- 15 is not very durable.

Another solution is to add antistatic or antifouling agents into the polymerization medium in order to reduce polymer build-up on the surfaces of the reactor. However, antistatic agents tend to interfere with the polymerization or reduce the activity of the

20 polymerization catalysts, because these agents have to be added in considerable amounts. Many fouling preventing agents are at the same time catalyst poisons and therefore they can be used only in relatively small amounts. Furthermore, antifouling agents remain in the end product and may thus impair the product quality.

- 25 Another solution is to cover reactor surfaces with a compound which forms a coating on the surface of the reactor. For example in PCT application WO93/23436 a coating of polyaniline is disclosed. However, polyaniline is very difficult to prepare and apply on the surfaces of the reactor and the cost of polyaniline is very high. In EP-patent 0 307 074 a process is disclosed, which comprises production of emulsion, dispersion, latex or bead
- 30 polymers in a water medium in a polymerization reactor, where some or all reactor surfaces exposed to gaseous or liquid monomers are coated with a film of oleophobic hydrophobic fluoropolymer material.

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The requirements for reactor coating for preventing polymer build-up are, among others, solubility in at least some common hydrocarbon, which is not harmful for the environment and which do not bear a health risk for workers. Further it may preferably be fillable with a component, which imparts the polymer antistatic properties. Still further it must be sprayable or paintable on the reactor wall, also when filled. Finally, the coating must withstand the reactor conditions (especially high temperatures, different liquid or gaseous mediums), give a smooth surface and give a good adhesion to the reactor wall or other surfaces.

According to the invention a new material for antifouling coatings have been found, which fulfills the requirements above. Thus one object of the invention is to achieve an antifouling coating, which can be applied to all kinds of steel vessels, reactors and pipes, where chemical inertness, smoothness and antistatic properties are important and which are exposed to substances causing fouling of the surfaces. Another object of the invention is to achieve an antifouling coating, which can be applied on the surfaces of reactors and equipment for polymerization or post-polymerization in order to prevent fouling of the surfaces. Still another object of the invention is to achieve a polymer coating, which can be filled with antistatic agents or antisheeting compounds. Still another object of the invention is to achieve a polymer coating which can be applied easily on surfaces of reactors and other equipment and which can be easily removed, when necessary.

The objects above can be achieved according to the invention by applying on the surfaces of reactors or other equipment a coating selected from polysulfone (PS) and polyetherimide (PEI) polymers.

25

Polysulfone polymers are a class of amorphous thermoplastic polymers characterized by high glass-transition temperatures, good mechanical strength, stiffness and thermal and oxidative resistance. These polymers are characterized by the presence of the para-linked diphenylsulfone group as part of their backbone repeat units. The basic repeat unit of any polysulfone always contains sulfone, aryl and ether units as part of the main backbone structure. Other commonly used name is polyethersulfone (PES). Polyether sulfone has good high temperature properties. It can easily be dissolved in N-methyl-2-pyrrolidone (NMP). It can easily be filled by compounds imparting the product antistatic properties.

Further it is important that the coating according to the invention can be easily painted or sprayed on the surfaces also when it is filled. Further it can be applied to all kinds of steel surfaces of reactors, lines etc. to form a coating, which is chemically smooth and chemically inert. Polyetherimide have same kind of properties.

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The thickness of coatings applied can be from 0.1 to 3 mm. The thickness required depends on the application and the environment, especially the temperature and pressure. In some applications the conditions are mild and therefore coatings having a thickness of 0.1-0.5 mm are adequate. In liquid type polymerization reactors the temperature is usually 20-80 °C, seldom higher. In gas phase reactors higher temperatures can be used and therefore greater thicknesses can be necessary.

The coatings according to the invention are based on polyether sulphone or polyetherimide dissolved in a proper solvent. A preferable solvent for PES is N-methyl-2-pyrrolidone, while also any other solvent capable of dissolving these polymers at a sufficient degree to achieve a coatable solution can be used. The polymer is dissolved in the solvent at an amount which depends on application method and the thickness desired. Thus the PES concentration in the solution can vary between 2-500 g/l. When the coating is applied by painting, more concentrated solutions can be used. When thinner coatings are formed or the coating is applied by spraying, a less concentrated solution can be used.

After spraying the solution on the surfaces being treated the solvent is removed in a conventional way.

According to a preferable embodiment of the invention the antistatic properties can be increased by adding antistatic agents or any component that increases the conductivity in the matrix of polymer. Such antistatic agent can be an inert component giving antistatic properties to the coating or it can be a component which is delivered from the coating gradually.

30

The antistatic agent can be any component which increases the electric conductivity of the polymer. The amount of an antistatic agent can be 0-50 w-%, preferably 5-30 w-% based on the coating solution. Suitable components are carbon black, chromium and other metal

powders or metallized mineral fillers. Also other known antistatic agents applied on surfaces to prevent antifouling can be used in polyether sulphone matrix, because it has excellent adhesion to steel and other metal surfaces and can therefore fix other antistatic agents to the surface treated.

5

The invention is applicable to reactors such as batch reactors, continuous stirred tank reactors or loop reactors, and gas phase reactors. Further the invention is also applicable to inlets and outlets of polymerization reactors as well as lines connecting reactors and other equipment, for example flash tanks, cyclones, silos etc.

10

The invention is further illustrated by the following examples.

#### Example 1

15 Steel plates were coated with solutions of polyether sulphone (PES) in N-methyl-2-pyrrolidone (NMP) by using various concentrations, coating thicknesses and various fillers. The solvent was removed by drying. These test samples were used for cross-cut tests to study the performance of the coatings.

20 Cross-cut tests were carried out according to DIN 5351. A needle was used to introduce 6 long cuts in the PES layer at a distance of 4 mm and 6 additional cuts were applied at a right angle to the first ones. The cuts were made in the same way (same force, same speed). The tests were carried out at two different places of the test plate. The size of the test plates was 140x140x4 mm.

25

After the cuts were finished the plates were brushed by means of a smooth brush. The appearance of the cross-cut field and a comparison with pictures and descriptions were the base for the evaluation of the test (scale 0-5, zero-value the best).

30 The filler used was carbon black. The results are presented in Table 1.

Table 1

	Coating solution concentration g/l	Coating thickness mm	Concentration of filler w-%	Cross-cut value
5	200	0.5	-	0.4
	200	1.0	-	0
	200	1.5	-	1
	500	0.5	-	0.6
10	500	1.0	-	0
	500	2.0	-	1
	200	1.5	5	1
	200	1.5	10	1
	200	1.5	15	1
15	200	1.5	20	1
	200	1.5	25	1
	200	1	5	0
	200	1	10	0
	200	1	15	0
20	200	1	20	1
	200	1	25	0
	200	0.5	5	0
	200	0.5	10	0
	200	0.5	15	0
25	200	0.5	20	0
	200	0.5	25	0
	500	0.5	5	0
	500	0.5	10	0
	500	0.5	15	0
30	500	0.5	20	0

As Example 1, but chromium powder was used as the filler instead of carbon black. The concentration of the coating solution was 500 g/l. The test results are presented in Table 2.

5 Table 2

	Coating thickness mm	Concentration of filler w-%	Cross-cut value
10	0.5	5	0
	0.5	15	0
	0.5	30	0
	1.0	5	0
	1.0	15	1
	1.0	30	1
15	1.5	5	1
	1.5	15	0
	1.5	30	3

## 20 Example 3

Steel plates were coated with a solution of PES in NMP. The concentration of the coating solution was 500 g/l and the amount of the carbon black acting as antistatic agent was 15 w-%. The coating thickness was 0.5 mm.

25

The test plates were aged in a hydrogen/ethylene atmosphere at 100 °C for 12 days. The ratio of hydrogen to ethylene was 1:10.

The cross-cut values were 0 almost in all tests. This example as well as examples 1-2  
30 show that the coatings are resistant and survive also at conditions typical of olefin polymerization.



## Example 4

In order to study the paintability or sprayability of PES solutions the zero-shear viscosity at various concentration was measured at 25 °C. The results are presented in the following

5 Table 3.

Table 3

	Concentration of coating solution g/l	Zero-shear viscosity Pas
10	1	0.0029
	5	0.0032
	10	0.0041
	11	0.005
	40	0.01
15	80	0.016
	100	0.031
	200	0.12
	300	0.14
	400	1.6
20	600	4.8

## Example 5

25 Shear viscosity was measured as in Example 4 but the concentration of coating solution was 500 g/l and the solution contained additionally carbon black. The results are presented in the following Table 4.

Table 4

	Content of filler w-%	Shear viscosity at 20 °C Pas	Shear rate 1/s
5	5	8	0.033
	5	7.1	0.07
	5	6.6	1
10	30	12000	0.0004
	30	500	0.03
	30	100	0.25
	30	50	1
	30	26	2

- 15 The examples 4 and 5 show that PES-solutions are paintable or sprayable as such and if fillers are added the viscosity of the solution can easily be lowered by applying shear forces.

#### Example 6

20

Volume resistivity measurements of test samples were carried out according to DIN 53482 VDE 0303 Teil 3. The test samples were cylinder-like having a diameter of 100 mm and a thickness of about 3 mm. The carbon black content was varied between 5 w-% and 20 w-%. The results are presented in Table 5.

25

Table 5

	Carbon black content (w-%)	Volume resistivity Ohm x cm
30	5	$10^9$
	10	$10^7$
	15	$10^6$
	20	$10^4$

## Examples 7-8

According to Example 3 steel plates were coated with a solution of polyetherimide (PEI) in N-methyl-2-pyrrolidone. The concentration of polyetherimide, antistatic agent and concentration and the thickness of coating were varied. As the antistatic agent carbon black (Flammruss 101) was used.

The compositions and properties of the coatings are presented in Table 6.

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Table 6

Example	PEI-concentration g/l	Antistatic agent	Thickness of coating mm	Volume resistivity Ohm x cm	Adhesion strength (pull-off) MPa
7	200	Carbon black 63.7 vol-%	0,5 (sprayed)	$2 \times 10^4$	1.3
8	500	"	1,0 (painted)	not measured	0,8

15

## Claims

1. An antifouling coating for reactors, vessels, lines or other equipment, which are exposed to gaseous or liquid monomers or polymer powders, **characterized in** that said  
5 coating comprises a polymeric coating selected from polysulfone (PS) and polyetherimide (PEI) polymers.
2. An antifouling coating according to claim 1, **characterized in** that polysulfone polymer is polyethersulfone (PEI).
- 10 3. An antifouling coating according to claim 1 or 2, **characterized in** that it has a thickness of 0.1-3 mm, preferably 0.3-2 mm.
4. An antifouling coating according to claims 1-3, **characterized in** that coating is filled  
15 with one or more substance giving antistatic properties.
5. An antifouling coating according to claim 4, **characterized in** that the amount of the substance is 1-50 w%, preferably 5-30 w%.
- 20 6. An antifouling coating according to claims 4-5, **characterized in** that said substance is carbon black.
7. An antifouling coating according to claims 4-5, **characterized in** that said substance is chromium powder.
- 25 8. An antifouling coating according to claims 4-5, **characterized in** that said substance is a metallized mineral filler.
9. A method for forming an antifouling coating on the surfaces of reactors, vessels, lines  
30 or other equipment exposed to liquid or gaseous monomers or polymer powders **characterized in** that said surfaces are coated with a polymeric coating selected from polysulfone and polyetherimide polymers.

10. A method according to claim 9, **characterized in** that polysulfone polymer is polyethersulfone (PES).

11. A method according to claims 9-10, **characterized in** that said coating is applied on  
5 the surfaces as solution.

12. A method according to claims 9-11, **characterized in** that said coating is applied by spraying or painting.

10 13. A method according to claims 9-12, **characterized in** that N-methyl-2-pyrrolidine (NMP) is used as solvent.

14. A method according to claims 9-13, **characterized in** that the solution is filled with one or more substances giving antistatic properties.

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15. A method according to claim 14, **characterized in** that said antistatic agent is carbon black.

16. A method according to claim 14, **characterized in** said antistatic agent is chromium  
20 powder.

17. A method according to claim 14, **characterized in** said antistatic agent is a metallized mineral filler.

25 18. Reactors, vessels, lines, silos, flash tanks or other equipment, which have surfaces exposed to liquid or gaseous monomers or polymer powders, **characterized in** that said surfaces are treated with methods according to any of the claims 9-17.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 97/00404

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09D 5/16, C08F 2/00, C23F 15/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F, C23F, C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	File WPI, Derwent accession no. 77-40988, TOA GOSEI CHEM IND LTD: "Suspension polymerisation of vinyl chloride - in vessel coated with scale inhibiting compsn."; & JP,A,52053990, 770430	1-3,9-13,18
Y	--	4-8,14-17
X	File WPI, Derwent accession no. 77-80295, TOA GOSEI CHEM IND LTD: Suspension polymerisation of vinyl chloride - in which a triaryl-phosphonium cyclopentadienylide is coated onto inner walls"; & JP,A,52115889, 770928	1-3,9-13,18
Y	--	1-18

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5026795 A (JOHN P. HOGAN), 25 June 1991 (25.06.91), abstract; claim 1; column 2, lines 18-27  --	1-18
A	US 4957982 A (KENNETH R. GEDDES), 18 Sept 1990 (18.09.90), abstract  -- -----	1-18

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
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Patent document cited in search report			Publication date	Patent family member(s)	Publication date
US	5026795	A	25/06/91	NONE	
US	4957982	A	18/09/90	CN 1026002 B	28/09/94
				CN 1030591 A	25/01/89
				DE 3884539 D,T	17/03/94
				EP 0307074 A,B	15/03/89
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